KINETICS OF CATALYZED CARBON MONOXIDE-HYDROGEN REACTIONS

BY

WILLIAM MUNRO CAMPBELL

B.A.Sc., University of Toronto, 1938
M.S., Case Institute of Technology, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

URBANA, ILLINOIS

1950

KINETICS OF CATALYZED CARBON MONOXIDE-HYDROGEN REACTIONS

BY

WILLIAM MUNRO CAMPBELL

B.A.Sc., University of Toronto, 1938
M.S., Case Institute of Technology, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

URBANA, ILLINOIS

1950

ACKNOWLEDGMENT

The author gratefully acknowledges the guidance of Professor H. F. Johnstone, in the direction of this research.

R. UNIV.
BIBLIOTHEEK
LEIDEN

KINETICS OF CATALYZED CARBON MONOXIDE-HYDROGEN REACTIONS

Introduction

In the Fischer-Tropsch process, carbon monoxide and hydrogen react in the presence of a catalyst, usually cobalt or iron, to give hydrocarbons and either carbon dioxide or water, or both. The hydrocarbon product, in general, consists of an oil with small amounts of gas and wax, but the conditions greatly affect the composition. The hydrocarbons are principally olefins and paraffins with some branched chain compounds and small amounts of naphthenes and aromatics. The catalyst has a large influence on the relative amounts of water and carbon dioxide formed. Colbalt catalysts in general give a high H_2O : CO_2 ratio, while iron catalysts usually give a much lower ratio. Many mechanisms for these reactions have been suggested, but none is completely satisfactory. The present work deals with the reaction mechanism, particularly with its effect on the H_2O : CO_2 ratio.

Historical

Some fractions of the hydrocarbon product formed with a cobalt cataylst contain as much as fifty percent olefins, most of which have the double bond in the internal part of the molecule (1) (2). Smaller percentages of olefins are found in the higher boiling fractions. Iron catalysts produce considerably more olefins, and most of these have the double bond in the terminal position. Since the proportion of olefins produced by a cobalt catalyst increases as the space velocity increases, the olefins have been suggested as the primary hydrocarbon product (2).

According to the most widely accepted theory of the reaction mechanism, the carbon monoxide is considered to react with the catalyst forming a carbon-rich carbide, which is then reduced to form CH_2 radicals. The CH_2 radicals polymerize

and form $(CH_2)_n$ chains on the surface. Craxford (3) considers that the chain growth is terminated when the end CH_2 radical picks up a chemisorbed hydrogen from a metal active center, forms a CH_3 radical, and completes the paraffin molecule. The paraffin molecule so formed is then desorbed. Herington (4), on the other hand, considers that the chain is only attached to the surface through the two end carbon atoms, and that it can be removed from the surface without picking up a hydrogen atom. With this mechanism an alpha olefin would be the primary product.

At atmospheric pressure, cobalt catalysts maintain almost constant activity for several weeks, after which the activity drops rapidly (5). Furthermore, as the activity decreases the product contains a higher proportion of low molecular weight hydrocarbons. Two possible explanations for these observation are presented. (a) The active carbide decomposes slowly, depositing free carbon, and forming points on the surface beyond which the $(CH_2)_n$ polmer can not grow. This results in shorter chains and a product of lower average molecular weight. (b) Wax accumulates in the pores of the catalyst, and once these pores are filled, the reaction rate decreases. Hydrogen diffuses through the wax faster than carbon monoxide, so that at the catalyst surface the H_2 : CO ratio may be greater than in the gas stream, a change which would tend to give a higher percentage of low-boiling hydrocarbons.

Progressive poisoning of a cobalt catalyst with hydrogen sulphide at first slightly increases the yield of the oil and total hydrocarbons, and then these yields decrease rapidly (6). The explanation for these observations is based on the assumption that hydrogen sulphide destroys the chain-ending active centers. Thus, a small amount of poising results in a higher molecular weight product, while a larger amount results in such a high molecular weight product that it cannot be desorbed from the surface, which causes a drop in the activity.

It is generally agreed that water is the primary product in which the oxygen appears, and that any carbon dioxide found

is the result of the water gas shift reaction. Bashkirov and co-workers (7), using an iron catalyst, added water to the normal H_2 - CO feed, and found that the shift reaction takes place rapidly. Kolbel and Engelhardt (8) studied the reaction of carbon monoxide and steam over different cobalt and iron catalysts, and concluded that the relative amounts of water and carbon dioxide are dependent on temperature alone. Their catalysts, however, were not in the normal operating condition. Watanabe and co-workers (9) studied the effect of varying the H_2 : CO ratio, and found that the changes produced in the H_2O : CO_2 ratio were in the opposite direction to that which would be expected from a consideration of the water gas equilibrium alone.

Experimental

The experiments were carried out in a tubular reactor using an iron catalyst. The catalyst consisted of a porous alundum tube, 0.5 inches I.D. by 24 inches long, with a 0.125 inch wall, impregnated with the active ingredients. This tube was packed into a 0.875 inch iron tube, which in turn was immersed in a bath of molten potassium nitrate and sodium nitrite. One end of the iron tube contained a glass tube which was packed with glass beads and served as a preheater. The product gases, freed from condensed matter, were collected in a calibrated constant pressure gasometer.

The catalysts were made by first impregnating the alundum tube with a molten mixture of ferric nitrate, copper nitrate and potassium carbonate. The catalyst mixture had an Fe : Cu ratio of 6:1 and contained 0.15% potassium carbonate. After impregnation, the nitrates were decomposed by heating the tube at a temperature which increased slowly from 120°C to 250°C, and then rapidly to 390°C. The oxide catalyst was pretreated, in general, with carbon monoxide for about forty hours, while the temperature was raised from 180° to 250°C.

Hydrogen and carbon monoxide mixtures were made up in the correct proportion, analyzed, and then passed over the cata-

lyst at accurately measured rates of 0.75 - 0.80 liters per hour. The product gases were analyzed for carbon dioxide by a gravimetic method, and for olefins, hydrogen, carbon monoxide, paraffins and nitrogen with a standard Fischer Gas Analyzer. From the analyses and the flow rates, the conversions and carbon, hydrogen and oxygen balances were calculated.

The following studies were made: (1) Effect of pretreatment of the catalyst; (2) Study of the reaction order at 245°C; (3) Effect of use at 280°C and at 250°C on the catalyst activity; (4) Effect of poisoning with hydrogen sulphide; (5) Comparison of activities of several catalysts for the shift reaction; and (6) Influence of the H_2 : CO ratio on the H_2O : CO_2 ratio.

Conclusions

The principal conclusions reached in the work are:

(1) Inactive catalysts are usually obtained when mixed nitrates are converted to the oxides by heating, and the oxides are treated with carbon monoxide at 0.1 atmospheres pressure and 325°C.

(2) After an initial period, similar behaviors are obtained with catalysts made by pretreating the oxides with hydrogen, carbon monoxide, or hydrogen plus carbon monoxide at temperatures from 190° to 270°C, or with steam plus hydrogen at 400°C followed by carbon monoxide at 190° to 270°C. This shows that the catalyst surface reaches a steady state condition with the reacting gases.

(3) The reaction does not appear to follow a simple zero, or first order process.

(4) At 280°C, the catalyst activity decreases rapidly with use, and soon reaches a constant activity where the principal products are methane, ethylene, carbon and carbon dioxide.

(5) At 250°C, the activity decreases slowly with use.

(6) The activity of the catalyst decreases linearly with the

amount of hydrogen sulphide absorbed, and when about 0.5 atoms of sulphur per atom of metal have been absorbed the activity reaches zero. The loss in activity is probly due to the reaction of sulphur with the metal active centers.

(7) Partial regeneration of a sulphur-poisoned catalyst can be effected by passing a pure hydrogen-carbon monoxide mixture over it. This recovery may be due to (a) the hydrogenation cracking of the surface $(CH_2)_n$ polmer, and the freeing of some metal active centers, or (b) the existence of two simultaneous hydrocarbon-forming reactions, one of which is only temporarily poisoned with hydrogen sulphide.

(8) The normal carbon dioxide-producing synthesis catalyst is very active for the shift reaction.

(9) Two types of active surfaces must be present in a normal catalyst. One of these, probly a carbide, catalyses the synthesis reaction, while the other, probably the metal itself, catalyzes the shift reaction.

(10) The synthesis reaction surface is destroyed by hydrogen sulphide poisoning and by heating at 310°C.

(11) The shift reaction surface is destroyed by hydrogen sulphide poisoning, but is almost unchanged by heating at 310°C.

(12) The activity of a carbon dioxide-producing catalyst can be increased by treatment with steam and carbon monoxide at 250°C. This effect is probably caused by oxidation of the metal active centers with the steam, followed by carbiding with carbon monoxide.

(13) The normal concentration of metal active centers in a water-producing catalyst is small, but this concentration can be increased by reduction with hydrogen. Thus, a water-producing catalyst will form more carbon dioxide when the reacting gas contains a high concentration of hydrogen.

(14) The Fischer-Tropsh reactions can be explained most satisfactorily by assuming that two hydrocarbon-forming reac-

tions take place simultaneously on the carbided surface. One reaction produces alpha olefins by simply splitting the polymer chain off the surface, while the other produces paraffins by hydrogenating the end of the $(CH_2)_n$ chain at a metal active center.

(15) In a carbon dioxide-producing catalyst, the metal active centers must exist as clusters, rather than as a uniform distribution over the carbided surface.

BIBLIOGRAPHY

1. Fischer, F., *Petroleum Refiner* 23, No. 2, 112-118 (1944)
2. Anderson, R. B., Krieg, A., Seligman, B., and O'Neill, W. E., *Ind. Eng. Chem.* 39, 1548-54 (1947)
3. Craxford, S. R., *Trans. Faraday Soc.* 35, 946-58 (1939)
4. Herington, E. F. G., *Trans. Faraday Soc.* 37, 361-6 (1941)
5. Anderson, R. B., Hall, W. K., Krieg, A., and Seligman, B., *J. Am. Chem. Soc.* 71, 183-8 (1949)
6. Herington, E. F. G., and Woodward, L. A. *Trans. Faraday Soc.* 35, 958-66 (1939)
7. Bashkirov, A. N., Kryukov, Y. B., and Kagan, Y. B., *Doklady. Akad. Nauk. SSSR*, 67, 1029-31 (1949)
8. Kolbel, H., and Engelhardt, F., *Erdol u. Kohle* 2, 52-9 (1949)
9. Watanabe, S., Morikawa, K., and Igawa, S., *J. Soc. Chem. Ind. Japan.* 38, suppl. binding, 328-31 (1935)

VITA

William Munro Campbell was born on January 21, 1915 near Glencoe, Ontario, Canada. After attending Alvinston and Glencoe High Schools, he graduated with a Senior Matriculation from the latter in 1932. Two years later he entered the University of Toronto, and graduated from there with Honors in Chemical Engineering in 1938. The next two years were spent in graduate study at the Case Institute of Technology, during which he held a teaching assistantship. He received the Degree of Master of Science in Chemical Engineering from this institution in 1940. For the next year and a half he held the Research Fellowship in Gas at the Ontario Research Foundation, Toronto, and in December 1941 he joined the Plant Research Department of Shawinigan Chemicals, Shawinigan Falls, Quebec. After more than four years of research work in this organization he left there in September 1946 to become Assistant Professor in Chemical Engineering at Queen's University, Kingston, Ontario. A year later he came to the University of Illinois as a part time Instructor in Chemical Engineering. Since then he has continued his graduate work in Chemical Engineering.